Unclassified   DTIC FILE COPY   (2)

AD-A202 389

DOCUMENTATION PAGE

	1b RESTRICTIVE MARKINGS
	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public release; distribution unlimited
4 PERFORMING ORGANIZATION REPORT NUMBER(S)	5 MONITORING ORGANIZATION REPORT NUMBER(S) R&D 5845-CH-01

DTIC SELECTED DEC 0 1 1988 D

6a. NAME OF PERFORMING ORGANIZATION Universität Erlangen-Nürnberg	6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION USARDSG(UK)
6c. ADDRESS (City, State, and ZIP Code) Henkestrasse 42, D-8520 Erlangen, Germany		7b ADDRESS (City, State, and ZIP Code) Box 65 FPO New York 09510-1500
8a. NAME OF FUNDING/SPONSORING ORGANIZATION USARDSG(UK) ERO	8b OFFICE SYMBOL (If applicable) AMXSN-UK-RC	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAJA45-87-M-0526

8c. ADDRESS (City, State, and ZIP Code) Box 65 FPO New York 09510-1500	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
	61103A	1L161103BH57	05	

11 TITLE (Include Security Classification)

(U) Polyfunctionalization of Cage Hydrocarbons

12 PERSONAL AUTHOR(S)
P. von Rague Schleyer

13a TYPE OF REPORT FINAL	13b TIME COVERED FROM Nov 87 TO Aug 88	14 DATE OF REPORT (Year, Month, Day) 1988, August	15 PAGE COUNT 31

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Synthesis (chem), Chem reactions, Chem bonds, Energetic materials
07	03		
19	01		

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

This report details the work carried out at the University of Erlangen-Nürnberg aimed at the syntheses of polyhalogenated cage molecules, their isolation, characterization, and assessment as potential precursors to high density energy materials.
A variety of halogenation methods have been investigated and applied (sometimes in combination) to a number of different starting materials e.g. adamantane $C_{10}H_{16}$ 1, diamantane $C_{14}H_{20}$ 2, and norbornadiene dimer $C_{14}H_{16}$ 3. Photochlorination has been found to be the most effective method of introducing large numbers of halogens into these cage molecules and has been applied to a variety of starting materials, culminating in the synthesis of 1,3,5,7-tetrabromodecachloroadamantane 4 and the successful analysis of its structure by X-ray diffraction. This corresponds to over 87% halogenation. Relatively high degrees of functionalisation (70% and 50%) have been achieved for diamantane 2 and norbornadiene dimer 3 respectively. The synthetic work as well as the methods of
CONTINUED OVER

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☒ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert J. Campbell	22b TELEPHONE (Include Area Code) 01-409 4423	22c OFFICE SYMBOL AMXSN-UK-RC

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete

Unclassified

19. CONTINUED

separation and characterisation of the product mixtures are reported. The results of semi-empirical molecular orbital calculations on dodecachloroadamantanes '5 and of the X-ray structural analysis of (4) are discussed. (f))

DTIC
COPY
INSPECTED

A-1

ii

POLYFUNCTIONALISATION OF CAGE HYDROCARBONS

FINAL TECHNICAL REPORT

by

Prof. Dr. Paul von Ragué Schleyer

August 1988

United States Army
European Research Office of the U.S. Army
London, England.

Contract Number DAJA 45-87-M-0526

Institut für Organische Chemie
Universität Erlangen-Nürnberg
Henkestrasse 42
D-8520 Erlangen
Federal Republic of Germany

8 8 12

Abstract

This report details the work carried out at the University of Erlangen-Nürnberg aimed at the syntheses of polyhalogenated cage molecules, their isolation, characterisation, and assessment as potential precursors to high density energy materials.

A variety of halogenation methods have been investigated and applied (sometimes in combination) to a number of different starting materials e.g. adamantane $C_{10}H_{16}$ 1, diamantane $C_{14}H_{20}$ 2, and norbornadiene dimer $C_{14}H_{16}$ 3. Photochlorination has been found to be the most effective method of introducing large numbers of halogens into these cage molecules and has been applied to a variety of starting materials, culminating in the synthesis of 1,3,5,7-tetrabromodecachloroadamantane 4 and the successful analysis of its structure by X-ray diffraction. This corresponds to over 87% halogenation. Relatively high degrees of functionalisation (70% and 50%) have been achieved for diamantane 2 and norbornadiene dimer 3, respectively. The synthetic work as well as the methods of separation and characterisation of the product mixtures are reported. The results of semi-empirical molecular orbital calculations on dodecachloroadamantanes 5 and of the X-ray structural analysis of 4 are discussed.

Introduction

Since many cage hydrocarbons are readily available, e.g. through rearrangement, the goal of this research was to develop methods for the direct introduction of functional groups which can be converted into polynitro or similar compounds. While details have been provided before,[1-4] it is useful to summarise he objectives and our earlier results. This work has been carried out in cooperation with the chemists in the Dover N.J. Army laboratory and with Dr. G. Sollott who formerly was also at that location but now is employed by an independent contractor and is carrying out research at Villanova University. Their findings on the materials we provided are promising.
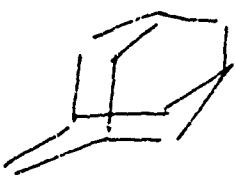
1
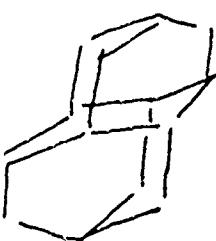
2

3

The synthesis of 1,3,5,7-tetranitroadamantane **6**[5] by Sollott and Gilbert provided the impetus for our work. These investigators found that 1,3,5,7-tetraiodoadamantane **7** could be converted via a photochemical Ritter reaction into derivatives of 1,3,5,7-tetra-aminoadamantane which in turn could be oxidised to give **6**. The tetraiodo compound **7** can be obtained from either 1,3,5,7-tetrabromo or -tetrachloroadamantane **9**, both of which can be prepared by ionic substitution reactions on adamantane itself. Hence, higher halogenated adamantanes (and other cage hydrocarbons) might be converted to corresponding polynitro compounds by similar procedures.
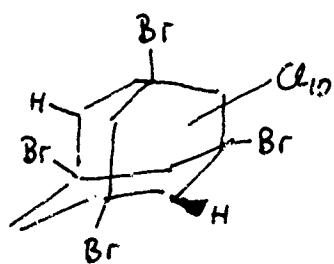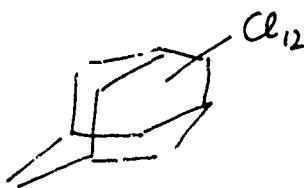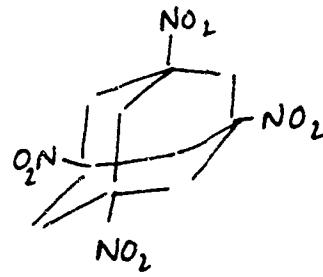
4 5 6
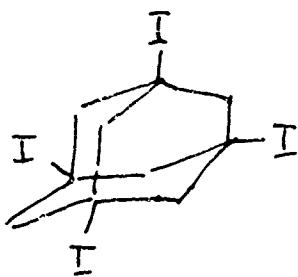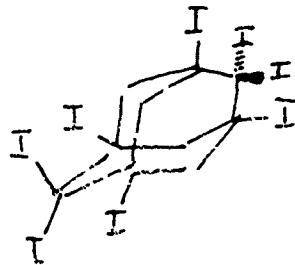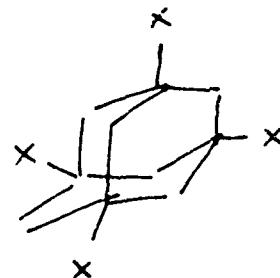
7 8 9

However, only four halogen atoms can be introduced directly under ionic reaction conditions emphasising the need for a more effective or complimentary procedure. Our previous findings indicated that photchlorination was superior to other methods e.g the use of transition metal catalysts, for this purpose. As detailed in previous reports[1-3] the distribution of the major product components from these photochlorination reactions (on adamantane **1**) depend on the reaction time, the solvent, and the substrate concentration, and could range from 4 to 10 chlorines per adamantane molecule. In the course of the work on the present contract this range has been successfully extended to 12 to 14 chlorines (or mixtures of chlorine and

bromine) for adamantane and a high degree of halogenation has also been achieved with diamantane 2, and norbornadiene dimer 3. Samples of these halogenated products totalling ca. 120g have been prepared and transmitted to the Dover laboratory. Conversion of the chlorines and bromines into iodines in these and other polyhalogenated materials has been demonstrated. However, difficulties with some samples also were found. To this end an alternative method of halogen exchange has been investigated at Erlangen and has been found to be applicable to a variety of halogenated adamantanes and diamantanes. In earlier work, Dr. Sollott was able to convert the octahaloadamantane mixture supplied by us into crystalline octaiodoadamantane which exhibited unexpected chemical reactions. These reactions can now be understood on the basis of an X-ray structure 8 which shows geminal diiodo units to be present. These units exhibit enhanced reactivity e.g. towards substitution, and provide potentially good sites for the introduction of nitrogen based fuctionalities. In the most recent work, our synthesis of adamantane wih 12-14 halogens (4,5) increased the proportion of geminal halogens and hopefully therefore further facilitates the introduction of the desired functional groups.

The disadvantage of free radical substitution reactions is their lack of selectivity. These are relatively exothermic processes with early transition states. Smith[5] has demonstrated that both bridgehead and secondary positions of adamantane are attacked. The inherent preference for bridgehead substitution is only partial, and must compete with the statistical (3:1) advantage for methylene attack. Therefore the polychlorination of adamantane not only produces mixtures with different numbers of chlorines, but also positional isomers corresponding to each composition as well. Partial separation of some of the product mixtures obtained from the photochlorination of 1,3,5,7-tetrachloroadamantane (9,X=Cl) has been achieved using HPLC.[4] As the degree of halogenation is increased to the 12-14 range, the number of possible positional isomers is reduced. A significant number remain however. The formidable computing facilities of the Institute for Organic Chemistry have allowed attempts to identify the individual isomers using mass spectrometry and NMR to be complimented by MNDO calculations on dodecachloroadamantane 5. This is found to be one of the major components of the product mixture when either adamantane 1 or 1,3,5,7- tetrachloroadamantane 9,X=Cl are photochlorinated.

Results

Percentage compositions given below are calculated by comparrison of the relative intensities of the (M·+ - halogen·) peaks in the mass spectra. ^{1}H NMR spectra are recorded on a JEOL PMX-60 spectrometer unless otherwise stated.   The results are presented and discussed in the following order:

(I)   Halogenation of diamantane 2.

(II)   Chlorination of norbornadiene dimer 3.

(III)   Bromination of adamantane 1, and 1,3,5,7-tetrabromoadamantane 9,X=Br.

(IV)   Photochlorination of adamantane 1.

(V)   Photochlorination of 1,3,5,7-tetrachloroadamantane 9,X=Cl.

(VI)   Photochlorination of 1,3,5,7-tetrabromoaamanatane 9,X=Br.

(VII)   X-ray structures of trifluoroiodo- and difluorodiiodoadamantane 15,16.

(VIII)   Photochlorination of 1,3,5,7-tetraiodoadamantane 9,X=I.

(IX)   Halogen exchange reactions (Br or Cl to I)

### (I)   Halogenation of diamantane 2

It was initially hoped to use tetrabromodiamantane 10 as a starting material for further photochlorin tion as it is readily synthesized under ionic reaction conditions. However, this compound is highly insoluble in solvents which can be employed in these photochlorinations dissolving only partially in hot CS_2 or THF. Hence, it was desirable to develop a selective synthesis for the more soluble 4,9-dibromodiamantane 11. The reaction conditions developed are mild and the yield consistently is over 60%. The procedure is as follows: a 250ml 3-necked round bottom flask fitted a pressure equalizing dropping funnel, a mechanical stirrer, and a reflux condenser summounted by a system of three gas traps. The first trap is filled with $CaCl_2$ to prevent moisture from entering the vessel and the remaining two are partially filled with water to absorb the HBr that is given off during the course of the reaction. Diamantane (37.6g, 0.2mol) is charged to the flask which is then cooled externally in an ice/salt bath. Bromine (40ml) is then added via the dropping funnel and a reaction ensues which is initially vigourous. After the reaction has slowed, the cooling bath is removed and the reaction mixture

allowed to warm to room temperature. It is then stirred at room temperature for a further 0.5hr before being cooled to -5°C again with the ice/salt bath. When the cooling is complete, iron (1.0g) is added in one portion and again the reaction becomes quite vigourous. The reaction is then allowed to slowly warm to room temperature and is stirred overnight. The solid product is dissolved in $CHCl_3$ and then added to a mixture of ice/HCl (200g/100ml). $NaHSO_3$ is added until the bromine colour is discharged, the organic phase separated, washed with water (X3) and dried over $MgSO_4$. Filtration and removal of the solvent under reduced pressure yields a white solid which after washing with petrol ether gives 60.4g (85%) 11.   Ionic chlorination of diamantane using $AlCl_3$ results in the formation of $C_{14}H_{16}Cl_4$ (analogous to 10) which is also found to be highly insoluble. Photochlorination results in a much higher degree of functionalisation. Reaction for 24hrs gave a product composition as follows;

$C_{14}H_{10}Cl_{10}$ 45%, $C_{14}H_9Cl_{11}$ 45%, $C_{14}H_8Cl_{12}$ 9%, $C_{14}H_7Cl_{13}$ 1%.

10   11
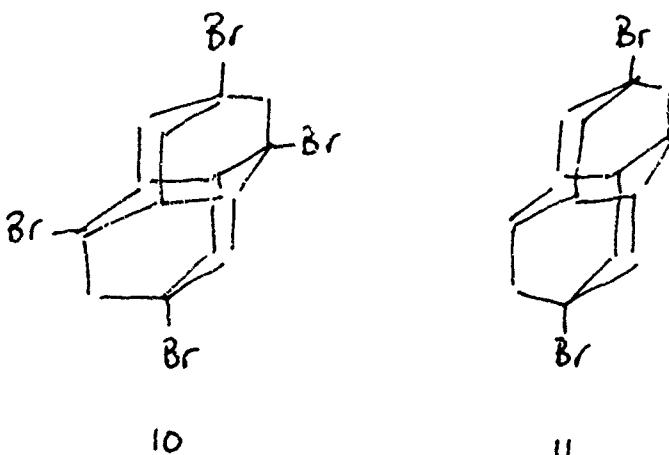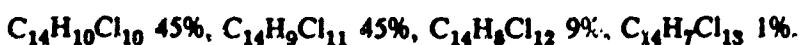
(II) Chlorination of norbornadiene dimer 3.

Ionic chlorination of 3 results in products in the Cl_4-Cl_7 range. The composition estimated from the mass spectrum is as follows:

$C_{14}H_{12}Cl_4$ 35%, $C_{14}H_{11}Cl_5$ 56%, $C_{14}H_{10}Cl_6$ 9%.

Photochlorination of 3 proceeds to a greater degree yielding products in the Cl_6-Cl_{10}

range. The Cl_9 compound precipitates from the solution and is therefore a bottleneck. The estimated composition of the mixture is:

$C_{14}H_8Cl_8$ 6.5%, $C_{14}H_7Cl_9$ 81%, $C_{14}H_6Cl_{10}$ 12.5%.

**(III) Bromination of adamantane 1 and 1,3,5,7-tetrabromoadamantane 9,x=Br.**

The bromination of adamantane under ionic conditions can be controlled to yield adamantanes selectively substituted with 1-4 bromines. Photobromination of adamantane in contrast to photochlorination does not proceed further than the Br_4 level. Attempts to brominate 9,X=Br, further by a variety of methods failed. Details are given in a previous report.[4]

(IV) Photochlorination of adamantane 1.

Photolysis for 20hrs gives a product mixture of the following composition;

$C_{10}H_4Cl_{12}$ 68%, $C_{10}H_3Cl_{13}$ 29%, $C_{10}H_2Cl_{14}$ 3%.

Attempted recrystalisation of this mixture from diethylether yields a colourless material which forms a plastic crystalline phase. X-ray investigations confirm that the material is crystalline and appears to belong to the cubic system. However, attempted solution of the structure failed due to the severe disordering. The adamantane molecule when surrounded by a sheath of chlorine atoms produces a highly symmetrical sphere-like structure which has little or no dipole moment which can direct the molecules in crystal packing. Hence, the orientation of the individual molecules within the lattice relative to each other is not fixed. The formation of such a plastic crystalline phase is common for molecules of high symmetry[7] and this is the reason for our failure, even with a good data set, to solve the structure.   MNDO calculations on dodecachloroadamantane 5, the major component of the above mixture[4] show clearly the preference for the more highly symmetrical positional isomers, the C_s, S_6, and C_{3v} isomers 12,13,14 being favoured by 5 kcal/mol over any C_1 point-group structure.
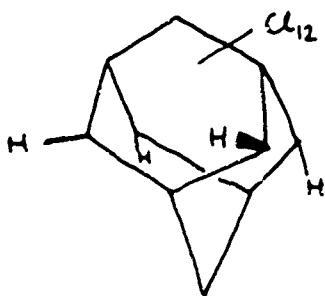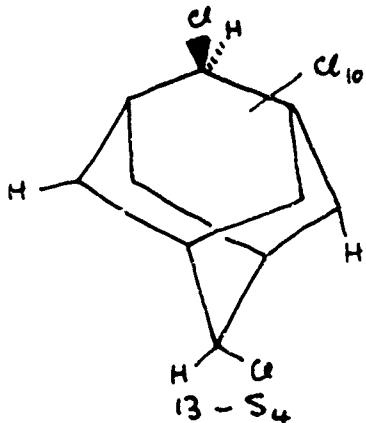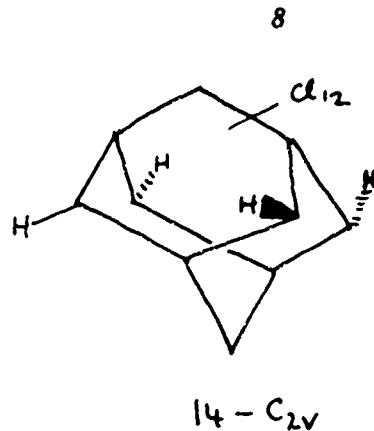
12 - C_s 13 - S_4 14 - C_{2v}

ISOMER   RELATIVE ENERGY kcal/mol

C_s	0.0
S_4	1.0
C_{2v}	1.9
all C_1	>6.8

(V) Photochlorination of 1,3,5,7-tetrachloroadamantane 9,X=Cl.

Short term photolysis of 9, X=Cl results in the formation of a mixture of Cl_5 and Cl_6 compounds, as is shown by the ^{1}H nmr spectrum (m,3.3; m,5.2ppm). Photolysis for 52hrs results in further chlorination. The product is found to contain a mixture of the Cl_{12}-Cl_{14} compounds characterised by the ^{1}H nmr spectrum (m,3.6 CH_2; m,5.8 CHCl). Recrystallisation of this mixture from diethyl ether yields a colourless material which X-ray analysis also shows to belong to the cubic system (cf. IV above). Unfortunately, a plastic crystalline phase problem was encountered again and structure solution was impossible. Much effort was expended on the attempted separation of this mixture using HPLC and the identification of the fractions obtained using 400MHz nmr. Details are provided in a previous report.[4]

(VI) Photochlorination of 1,3,5,7-tetrabromoadamantane 9,X=Br.

It is clear that if disordered crystals are to be avoided, the molecules must have at least local dipoles or must crystallise with a polar solvent trapped in the lattice. Hence, it was hoped that photochlorination of 9,X=Br and recrystallisation of the products from a solvent which acts as a good ligand would result in a more ordered structure. Indeed, success was achieved from a sample prepared by 48hrs photochlorination of the tetrabromo- compound. This

resulted in a product mixture with the following approximate composition;

$C_{10}H_4Br_4Cl_8$ 40%, $C_{10}H_3Br_4Cl_9$ 40%, $C_{10}H_3Br_5Cl_8$ 5%, $C_{10}H_2Br_4Cl_{10}$ 15%.
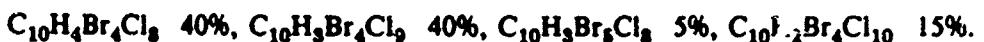
Recrystallisation from THF:diethyl ether (1:5) by dissolving the mixture in hot THF and adding the ether resulted in colourless crystals which did not exhibit the previously mentioned disordering. The crystals have monoclinic symmetry and belong to the space group $P2_1/n$ with cell dimensions a=929.3(6), b=1008.7(8), c=2502.3(15) pm, β=97.92°, V=2328 x10⁶ pm³, density$_{calc.}$=2.48 g/cm³ (Z=4). The R-value was 0.089, R_w=0.087, and 189 parameters were refined. The structure was solved with direct methods (SHELXS-86) and the halogen atoms were refined anisotropically. The carbon and oxygen atoms were isotropically refined and the positions of the hydrogens calculated to give an ideal geometry. A total of 3240 reflections were measured providing an asymetric data set of 2168 reflections from which 1320 with F > 4σ were observed. The crystal decomposed rapidly during the data collection, so that only data up to 2θ=40° could be collected.   Further crystal structure data is provided Tables 1-5 along with plots of different views of the molecule (figures 1-3). Figure 1 gives the crystallographic numbering scheme, Figure 2 shows the positioning of the THF solvent molecule, and Figure 3 shows the C_2 symmetry of the structure when the THF is not taken into consideration. The structure is composed of $C_{10}H_2Br_4Cl_{10}$: THF units. We thus have introduced fourteen halogen substituents on to the adamantane molecule. All of these can potentially be converted into nitrogen-based functionalities. This would certainly be a milestone in the "high density" energy materials programme! The spherical nature of this species can be clearly seen from the two space filling plots (Figures 4 and 5) as can the interaction of the THF molecule wth one of the two "holes" in the spherical surface caused by the presence of the two remaining hydrogen atoms. The presence of THF, possibly due to hydrogen bonding[9], disturbs the high symmetry of the halogenoadamantane units. The local dipoles due to the differing electronegativities of the bromine and chlorine substituents also may provide anisotropic interactions between molecules and lead to greater order in the crystal lattice.   The stereo-views of the unit cell (figures 6 and 7) show how the relationship between different molecules within the crystal are being dictated by anisotropic interactions.

(VII) X-ray structures of trifluoroiodo- and difluorodiiodoadamantane 15,16.

These mixed halogen compounds were produced during general studies of halogen exchange, with specific reference as precursors of novel cations.[10] The most interesting features in the X-ray crystal structures of 15 and 16 are the solid state intermolecular interactions between iodine atoms and between iodine and fluorine atoms. These interactions between the different halogen atoms are sufficient to order the molecules in the crystal.

Trifluoroiodoadamantane 15, crystallises from light petrol in the monoclinic space group C 2/c with cell dimensions a=2394.9(7), b=733.4(2), c=2600.0(7) pm, β=93.43(2)°. There are two independant formula units in the assymetric unit. The molecules form centrosymmetric tetrameric aggregates with I-I and F-I non covalent interactions. The I-I distance is 3.730 Å, and I-F =3.312 Å which are both appreciably shorter than the sum of the van der Waals radii (4.3, and 3.5 Å respectively). 2266 reflections were observed with F>4σ(F). 265 parameters were refined to an R value R=0.082, K_w=0.086 (W=σ^2(F) + 0.0021 F²). Figure 8 shows the two independant fomula units, figure 9 the tetrameric units and figure 10, a stereo view of the unit cell. Difluorodiiodoadamantane 16, crystallises from light petrol in the monoclinic space group C 2/c with cell dimensions as follows: a=1257.5(4), b=1174.0(4), c=837.3(3) pm, β=95.75(3)°. The molecules reside in special positions and have crystallographic C_3 symmetry. They are connected in the crystal via I-F interactions I-F =3.326 Å. There are no short I-I distances. 1725 reflections with F>6σ(F) were used to refine 78 parameters. R=0.055, R_w =0.061 (W=σ^2F + 0.0001 F²). Figure 11 shows the structure of 16 and figure 12 the unit cell, with the I-F interactions indicated.

15

16
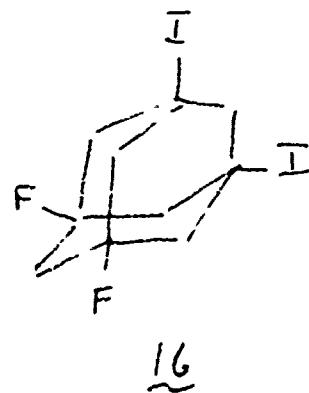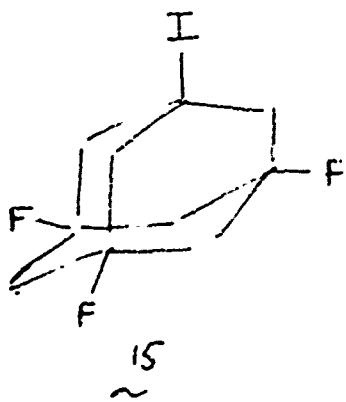
(VIII) Photochlorination of 1,3,5,7-tetraiodoadamantane 7.

Photochlorination for two hours results in the formation of 1,3,5,7-tetrachloroadamantane 9,X=Cl plus liberated iodine. The iodines are subst'·uted cleanly for chlorines. Further radical substitution is inhibited by the presence of the liberated iodine.

(IX) Halogen exchange reactions.

A modified halogen exchange[8] procedure has been developed at Erlangen. Using this method di-,tri-,and tetrachloroadamantane and di-,tri-, and tetrabromodiamantane have been converted into the corresponding iodo compounds in yields ranging from 60-80%. It is hoped to extend this to those cage molecules with higher degrees of halogenation. A typical procedure follows. A clean dry 500ml 3-necked flask fitted with a reflux condenser summounted by a $CaCl_2$ drying tube was charged with CS_2 (300ml) and aluminium foil (3.25g,1.16 $\times 10^{-1}$ mol) and the solution cooled with an ice bath. Iodine (44.16g, 0.174mol I_2) was then added in one portion. The temperature increased. After cooling, the reaction mixture was allowed to warm to room temperature and stirred for 30 mins., before being refluxed until the violet iodine colour turns to brown. After cooling the resulting solution of AlI_3 in CS_2 to 0-5°C with an ice/salt bath, 4,9-dibromodiamantane (20g, 5.78 $\times 10^{-2}$ mol) is added in one portion. The reaction mixture stirred at 0-5°C for 10 minutes and then poured into and ice/HCl mixture (500g/200ml). $NaHSO_3$ is added to discharge the brown colour, the organic phase washed with water (2X150ml), neutralised, washed again with water and dried over $MgSO_4$. The solvent is then removed under reduced pressure yielding a 4,9-diiododiamantane which can be recrystallised from diethyl ether in 65% yield.

Conclusions

Our previous objectives for the high density energy materials programme concentrated on introducing eight halogens into adamantane. The work reported above has resulted in a large increase (to fourteen) in the number of halogens which can be substituted consistantly. All of these halogen atoms can in principle be replaced by a nitro or similar nitrogen-based substituent. Chloroadamantanes with 12-14 chlorines can now be synthesised (as a mixture)

without problem and samples totalling 120g have been supplied to the scientists in the USA for further investigation. Features which polarise these otherwise mainly spherical molecules (mixed halogens or polar solvent) avoid the formation of plastic crystalline phases. The structures of several of these molecules have been solved by X-ray diffraction. Methods of separation of the different positional isomers in product mixtures by HPLC have been developed.[4] Computational methods have aided the interpretation of complex mass spectra[4] and given insight into the relative stabilities of the possible products.

References

1. 1st Periodic Report on Contract No. DAJA 45-85-C-0014.

2. 1st Annual and 2nd Periodic Report on Contract No. DAJA 45-83-C-0014. 3. 3rd Periodic Report on Contract No. DAJA-45-83-C-0014.

4. 1st and 2nd Periodic Reports on Contract No. DAJA 45-87-M-0526.

5. G.P. Sollott and E.F. Gilbert, *J.Org.Chem.*,1980,45,5405.

6. G.W. Smith and H.D. Williams, *J.Org.Chem.*,1961,26,2207.

7. E.F. Westrum Jr. *J.Chem.Educ.*,1962,39,443.
   S.S. Chang and E.F. Westrum Jr., *J.Phys.Chem.*,1960,64,1547.

8. For similar reactions see refs 5 and 6 and also J.W. McKinley, R.E. Pincock, W.B. Scott, *J.Am.Chem.Soc.*,1973,95,2030.

9. A. Allerhand and P.v.R. Schleyer, *J.Am.Chem.Soc.*,1963,85,1715.

10. M. Bremer, P.v.R. Schleyer, K. Schötz, M. Kausch, M. Schindler, *Angew.Chem.Int.Ed.Engl.*,1987,26,761.

Personell involved in this work

Prof. Dr. Paul von Rague Schleyer (Principal Investigator)
Dr. Peter S. Gregory (Post Doctoral Associate)
Dipl. Chem. Matthias W.W. Bremer (Graduate Student)

Tab. 1. Atomkoordinaten $(x10^4)$ und äquivalente isotrope Thermalparameter $(pm^2 \cdot 10^{-1})$

	x	y	z	U(eq)
Br(1)	-689(5)	5108(4)	5698(2)	67(2)
Br(2)	1362(4)	3?45(4)	7811(1)	58(1)
Br(3)	-3330(4)	575(4)	6556(2)	66(2)
Br(4)	2384(4)	184(4)	5945(2)	66(2)
Cl(1)	-834(11)	5215(9)	6972(4)	72(4)
Cl(2)	1916(11)	4969(10)	6762(4)	74(4)
Cl(3)	-2211(9)	2818(8)	7433(4)	55(4)
Cl(4)	-542(9)	574(9)	7589(3)	52(3)
Cl(5)	-1300(10)	-29(10)	5642(4)	67(4)
Cl(6)	-80(9)	-1016(8)	6613(4)	58(4)
Cl(7)	187(12)	2325(10)	5208(3)	74(4)
Cl(8)	2487(11)	3386(11)	5814(5)	91(5)
Cl(9)	-3288(16)	3631(17)	6237(7)	167(9)
Cl(10)	3467(9)	2161(10)	6964(4)	72(4)
C(1)	-310(29)	3518(30)	6153(11)	37(8)
C(2)	310(30)	3987(29)	6740(12)	37(9)
C(3)	529(27)	2740(27)	7063(11)	26(8)
C(4)	-880(29)	1896(30)	7110(11)	37(8)
C(5)	-1521(29)	1493(30)	6548(12)	35(8)
C(6)	-461(32)	511(32)	6275(13)	45(9)
C(7)	991(27)	1348(29)	6264(11)	29(8)
C(8)	805(31)	2603(31)	5907(12)	40(8)
C(9)	-1708(29)	2747(30)	6174(13)	39(9)
C(10)	1564(25)	1701(29)	6853(10)	23(7)
O(01)	-3648(44)	1930(44)	4765(16)	169(16)
C(01)	-3475(55)	3180(54)	4482(22)	138(20)
C(02)	-4698(59)	3437(65)	4204(24)	174(26)
C(03)	-5064(54)	1767(56)	4813(21)	142(21)
C(04)	-5758(63)	2798(57)	4402(22)	161(24)

* äquivalente isotrope U berechnet als ein Drittel der
  Spur des orthogonalen U_{ij} Tensors

Tab. 2. Bindungsabstände (pm)

Br(1)-C(1)	197.4 (30)		Br(2)-C(3)	200.1 (27)
Br(3)-C(5)	192.2 (28)		Br(4)-C(7)	198.6 (27)
Cl(1)-Cl(2)	268.3 (14)		Cl(1)-C(2)	177.6 (29)
Cl(2)-C(2)	178.7 (29)		Cl(3)-C(4)	181.4 (28)
Cl(4)-C(4)	179.4 (30)		Cl(5)-C(6)	176.4 (32)
Cl(6)-C(6)	177.2 (32)		Cl(7)-Cl(8)	268.7 (15)
Cl(7)-C(8)	179.5 (32)		Cl(8)-C(8)	179.2 (30)
Cl(9)-C(9)	174.2 (30)		Cl(10)-C(10)	181.6 (25)
C(1)-C(2)	158.2 (38)		C(1)-C(8)	156.9 (40)
C(1)-C(9)	152.0 (37)		C(2)-C(3)	149.6 (37)
C(3)-C(4)	157.8 (36)		C(3)-C(10)	155.6 (36)
C(4)-C(5)	151.4 (37)		C(5)-C(6)	160.6 (39)
C(5)-C(9)	157.0 (40)		C(6)-C(7)	159.5 (38)
C(7)-C(8)	154.6 (40)		C(7)-C(10)	154.8 (35)
O(01)-C(01)	146.5 (55)		O(01)-C(03)	134.6 (52)
C(01)-C(02)	128.4 (58)		C(02)-C(04)	132.2 (61)
C(03)-C(04)	154.8 (61)			

Tab. 3. Bindungswinkel (°)

C(2)-C(1)-Br(1)	108.2(20)	C(8)-C(1)-Br(1)	109.4(19)
C(8)-C(1)-C(2)	110.9(22)	C(9)-C(1)-Br(1)	110.1(19)
C(9)-C(1)-C(2)	109.7(24)	C(9)-C(1)-C(8)	108.7(25)
Cl(2)-C(2)-Cl(1)	97.7(15)	C(1)-C(2)-Cl(1)	110.3(19)
C(1)-C(2)-Cl(2)	113.8(20)	C(3)-C(2)-Cl(1)	117.2(21)
C(3)-C(2)-Cl(2)	113.0(20)	C(3)-C(2)-C(1)	105.1(23)
C(2)-C(3)-Br(2)	107.7(18)	C(4)-C(3)-Br(2)	107.3(18)
C(4)-C(3)-C(2)	115.8(23)	C(10)-C(3)-Br(2)	107.6(16)
C(10)-C(3)-C(2)	115.6(23)	C(10)-C(3)-C(4)	102.4(21)
Cl(4)-C(4)-Cl(3)	99.0(14)	C(3)-C(4)-Cl(3)	112.0(20)
C(3)-C(4)-Cl(4)	111.8(19)	C(5)-C(4)-Cl(3)	109.8(19)
C(5)-C(4)-Cl(4)	115.9(22)	C(5)-C(4)-C(3)	108.1(22)
C(4)-C(5)-Br(3)	111.4(19)	C(6)-C(5)-Br(3)	106.8(20)
C(6)-C(5)-C(4)	111.6(23)	C(9)-C(5)-Br(3)	111.1(18)
C(9)-C(5)-C(4)	109.8(25)	C(9)-C(5)-C(6)	105.8(22)
Cl(6)-C(6)-Cl(5)	101.6(17)	C(5)-C(6)-Cl(5)	110.2(20)
C(5)-C(6)-Cl(6)	115.5(21)	C(7)-C(6)-Cl(5)	115.4(21)
C(7)-C(6)-Cl(6)	110.4(20)	C(7)-C(6)-C(5)	104.2(24)
C(6)-C(7)-Br(4)	106.8(19)	C(8)-C(7)-Br(4)	106.5(18)
C(8)-C(7)-C(6)	114.1(23)	C(10)-C(7)-Br(4)	110.7(17)
C(10)-C(7)-C(6)	107.3(22)	C(10)-C(7)-C(8)	111.3(24)
Cl(8)-C(8)-Cl(7)	97.0(16)	C(1)-C(8)-Cl(7)	109.0(20)
C(1)-C(8)-Cl(8)	114.8(22)	C(7)-C(8)-Cl(7)	115.8(22)
C(7)-C(8)-Cl(8)	113.5(20)	C(7)-C(8)-C(1)	106.7(23)
C(1)-C(9)-Cl(9)	118.3(23)	C(5)-C(9)-Cl(9)	113.1(20)
C(5)-C(9)-C(1)	113.6(23)	C(3)-C(10)-Cl(10)	114.1(19)
C(7)-C(10)-Cl(10)	114.8(17)	C(7)-C(10)-C(3)	108.7(20)
C(03)-O(01)-C(01)	108.3(45)	C(02)-C(01)-O(01)	107.1(51)
C(04)-C(02)-C(01)	110.4(60)	C(04)-C(03)-O(01)	101.0(47)
C(03)-C(04)-C(02)	107.9(53)		

Tab. 4. Anisotrope Thermalparameter ($pm^2 \times 10^{-1}$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	101(3)	44(3)	58(3)	19(2)	22(2)	12(2)
Br(2)	76(3)	59(3)	38(2)	-9(2)	4(2)	-15(2)
Br(3)	46(2)	73(3)	82(3)	-6(3)	22(2)	-19(2)
Br(4)	69(3)	58(3)	78(3)	-6(2)	40(2)	21(2)
Cl(1)	111(8)	41(6)	71(7)	-2(6)	34(6)	15(6)
Cl(2)	94(7)	52(7)	77(8)	-2(6)	20(6)	-28(6)
Cl(3)	59(6)	51(7)	65(7)	-9(5)	45(5)	0(5)
Cl(4)	59(6)	49(6)	48(6)	18(5)	10(5)	-19(5)
Cl(5)	78(6)	67(7)	56(6)	-27(6)	14(5)	-14(6)
Cl(6)	70(6)	24(6)	83(7)	8(5)	24(5)	7(5)
Cl(7)	126(9)	69(8)	32(6)	1(5)	25(6)	16(7)
Cl(8)	88(8)	83(9)	110(10)	10(8)	51(7)	-13(7)
Cl(9)	123(11)	165(16)	218(18)	58(15)	46(12)	45(11)
Cl(10)	52(6)	74(8)	92(8)	0(6)	22(5)	-3(5)

der Temperaturfaktorexponent hat die Form:

$$-2\pi^2 (h^2 a*^2 U_{11} + \ldots + 2hka*b*U_{12})$$

Tab. 5. H-Atomkoordinaten ($\times 10^4$) und isotrope
Thermalparameter ($pm^2 \times 10^{-1}$)

	x	y	z	U
H(9A)	-1885	2470	5805	80(1)
H(10A)	1557	925	7075	80(1)
H(01A)	-2695	3086	4267	80(1)
H(01B)	-3244	3868	4744	80(1)
H(02A)	-4891	4371	4216	80(1)
H(02B)	-4638	3174	3839	80(1)
H(03A)	-5371	867	4747	80(1)
H(03B)	-5241	2024	5169	80(1)
H(04A)	-6311	2299	4122	80(1)
H(04B)	-6388	3396	4561	80(1)

NON-BONDED DISTANCES WITH TRANSFORMATIONS TO GENERATE SECOND ATOM

```
CL1  . BR'    3.209
CL2 ...BR1    3.375
CL7 ..BR1     3.209
CL8 ...BR1    3.406
CL9 ...BR1    3.267
C2  ..BR'     2.888
C8  ..BR'     2.900
C9  ...BR'    2.875
H9A ...BR1    2.909
BR' ...BR1    3.871    0.0000-X     1.0000-Y     1.0000-Z
CL7 ...BR1    3.510    3.0000-X     1.0000-Y     1.0000-Z
CL1 ...BR2    3.387
CL2 ...BR2    3.241
CL3 ...BR2    3.368
CL4  .BR2     3.233
CL10. BR2     3.244
C2  ..BR2     2.939
C4  ...BR2    2.893
C10 ...BR2    2.982
H10A. BR2     2.997
BR4 ...BR2    3.740    0.5000-X    -0.5000+Y     1.5000-Z
CL2  .BR2     3.755    0.5000-X     0.5000+Y     1.5000-Z
CL5 ..BR2     3.654    0.5000-X    -0.5000+Y     1.5000-Z
CL3  .BR3     3.234
CL4 ...BR3    3.429
CL5 ...BR3    3.195
CL6 ...BR3    3.407
CL9 ..BR3     3.185
CL10...BR3    3.534    1.0000+X     0.0000+Y     0.0000+Z
C4  ...BR3    2.848
C5  ..BR3     2.839
C9  ..BR3     2.887
CL3 ..BR3     3.753   -0.5000-X     0.5000+Y     .5000-Z
CL5  . BR4    3.421
CL6 ...BR4    3.231
CL7 ...BR4    3.364
CL8  .BR4     3.250
CL10 ..BR4    3.296
C5   .BR4     2.884
C8  ...BR4    2.843
C10 ...BR4    2.918
O01 ...BR4    3.098    0.0000-X     0.0000-Y     1.0000-Z
CL3 ..CL1     3.029
CL5 ...CL'    3.180
C1  ..CL1     2.758
C3  ...CL1    2.795
C9  ...CL1    3.231
CL3 ...CL1    3.616   -0.5000-X    -0.5000+Y     1.5000-Z
CL4 ..CL'     3.687   -0.5000-X    -0.5000+Y     1.5000-Z
CL8 ...CL2    2.961
CL10...CL2    3.190
C1  ...CL2    2.824
C3  ...CL2    2.742
C8  ...CL2    3.286
C10 ...CL2    3.322
CL4 ...CL2    3.609    0.5000-X    -0.5000+Y     1.5000-Z
CL4 ...CL3    2.744
CL9 ...CL3    3.145
C2  ...CL3    3.299
C3  ...CL3    2.815
C5  ...CL3    2.729
C9  ...CL3    3.241
CL4 ...CL3    3.474   -0.5000-X    -0.5000+Y     1.5000-Z
```

CL6	CL4	2.995			
C3		2.795			
C5		2.808			
C6	...CL4	3.297			
C10	..CL4	3.064			
H10A	...CL4	2.489			
CL6	...CL5	2.740			
CL7	..CL5	3.015			
C5	..CL5	2.765			
C7	..CL5	2.840			
C9	..CL5	3.315			
C9	...CL5	3.143			
H9A	...CL5	2.621			
CL7	...CL5	3.391	0.0000-X	0.0000-Y	1.0000-Z
C4	...CL6	3.309			
C5	...CL6	2.856			
C7	...CL6	2.766			
C10	...CL6	3.160			
H10A	...CL6	2.655			
C1	...CL7	2.743			
C7	...CL7	2.833			
C9	...CL7	3.189			
H9A	...CL7	2.582			
CL10	...CL9	3.152			
C1	...CL8	2.835			
C2	...CL8	3.313			
C7	...CL8	2.795			
C10	...CL8	3.307			
C1	...CL9	2.803			
C5	...CL9	2.764			
H9A	...CL9	2.141			
H02A	...CL9	2.782	-1.0000-X	1.0000-Y	1.0000-Z
C3	..CL10	2.832			
C7	..CL10	2.837			
H10A	...CL10	2.214			
C3	...C1	2.444			
C5	..C1	2.586			
C7	..C1	2.500			
H9A	..C1	1.925			
C10	..C1	2.952			
C4	...C2	2.603			
C9	..C2	2.595			
C9	..C2	2.536			
C10	..C2	2.583			
C5	..C3	2.504			
C7	...C3	2.523			
C8	...C3	2.938			
C9	..C3	2.852			
H10A	...C3	2.064			
C5	..C4	2.582			
C7	..C4	2.352			
C9	...C4	2.524			
C10	..C4	2.442			
H10A	...C4	2.479			
C7	..C5	2.526			
H9A	...C5	2.095			
C10	..C5	2.883			
C8	...C6	2.636			
C9	...C6	2.534			
C10	...C6	2.532			
C9	...C7	2.862			
H10A	...C7	2.077			
C9	...C8	2.510			
H9A	...C8	2.485			
C10	...C8	2.554			
H01A	...O01	1.993			

```
H01B...001    1.992
CO2  ..001    2.2'4
H03A...001    1.924
H03B ..001    1.893
CO4 ...001    2.237
-02A   CO'    1.845
H02B.. CJ1    1.826
C03  ..C01    2.280
CO4   .CC'    2.'4'
-0'B   H0'A   '.568
CO2  ..H01A   '.883
-02B. .H01A   1.985
CO2 ...H01B   1.842
-02A ..H01B   1.962
C03 ...C02    2.324
H04A...C02    1.880
H04B...CO2    '.895
H02B...H02A   '.568
CO4 ...H0.a   1.854
H04B...H02A   '.985
CO4  ..H02B   1.889
H04A...H02B   '.952
H04A.. C03    2.033
-04B...C03    2.'32
H03B...H03A   '.568
C04 ...H03A   2.'44
C04 ...H03B   2.073
H04B...H04A   1.568
```

Figure 1
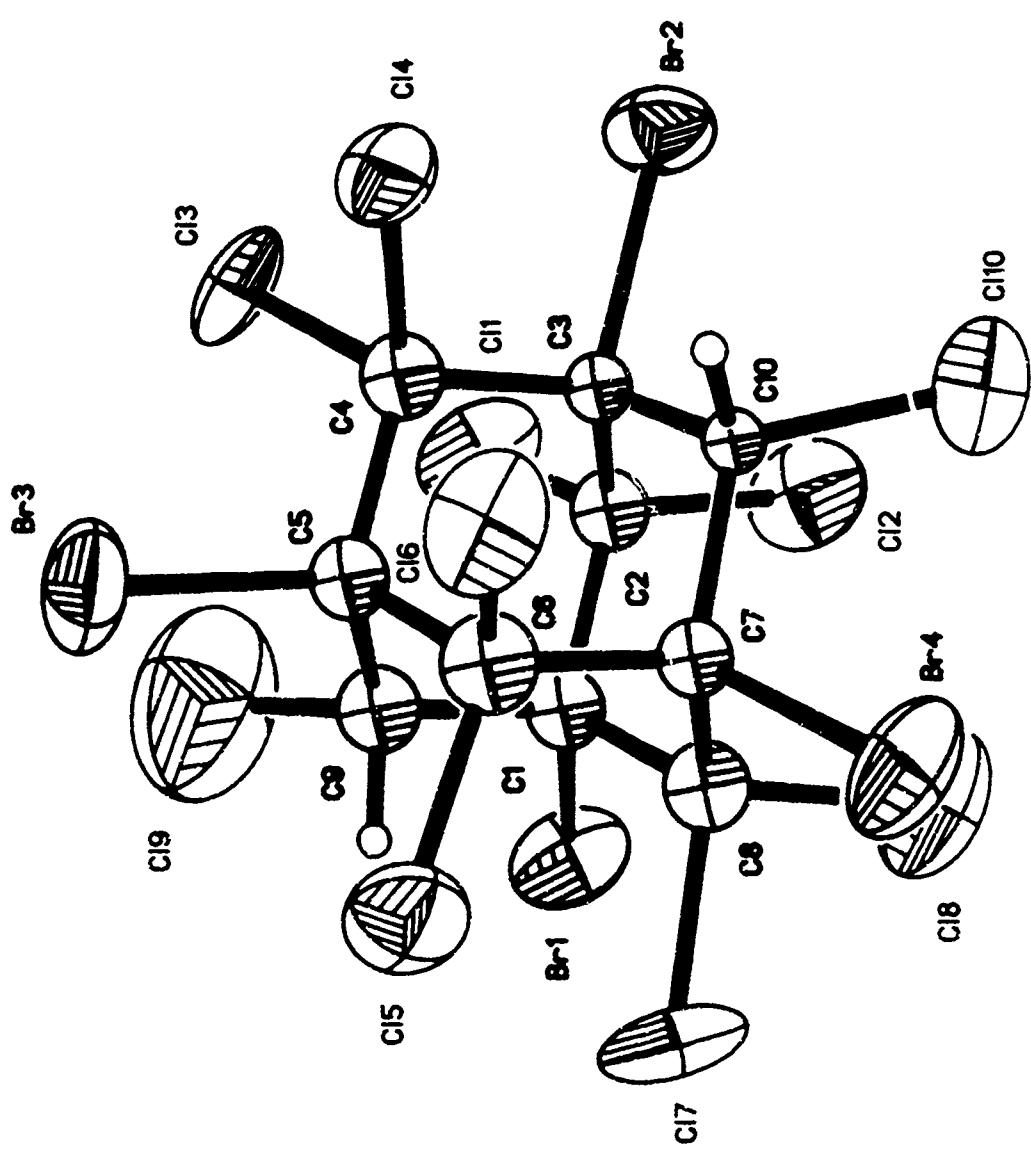
FIGURE 2
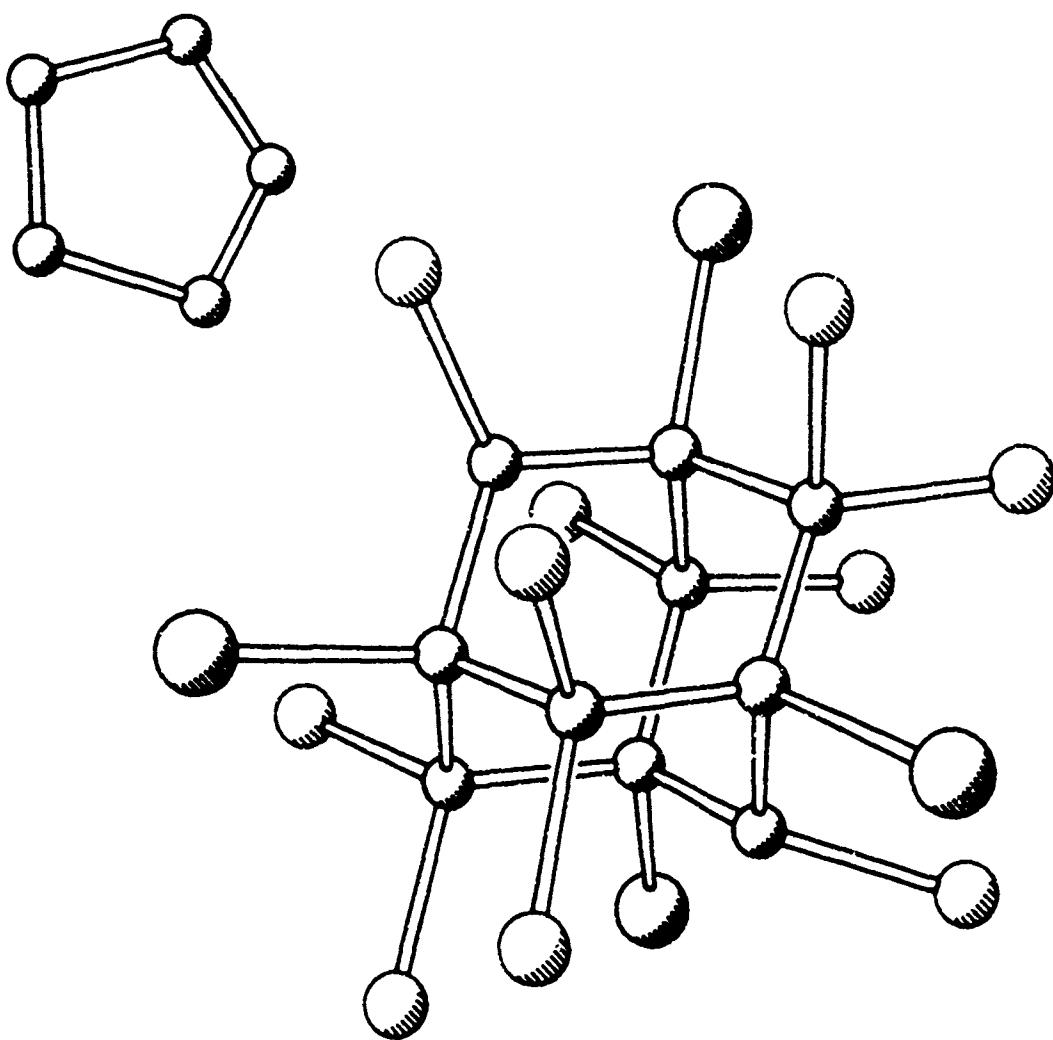
Figure 3
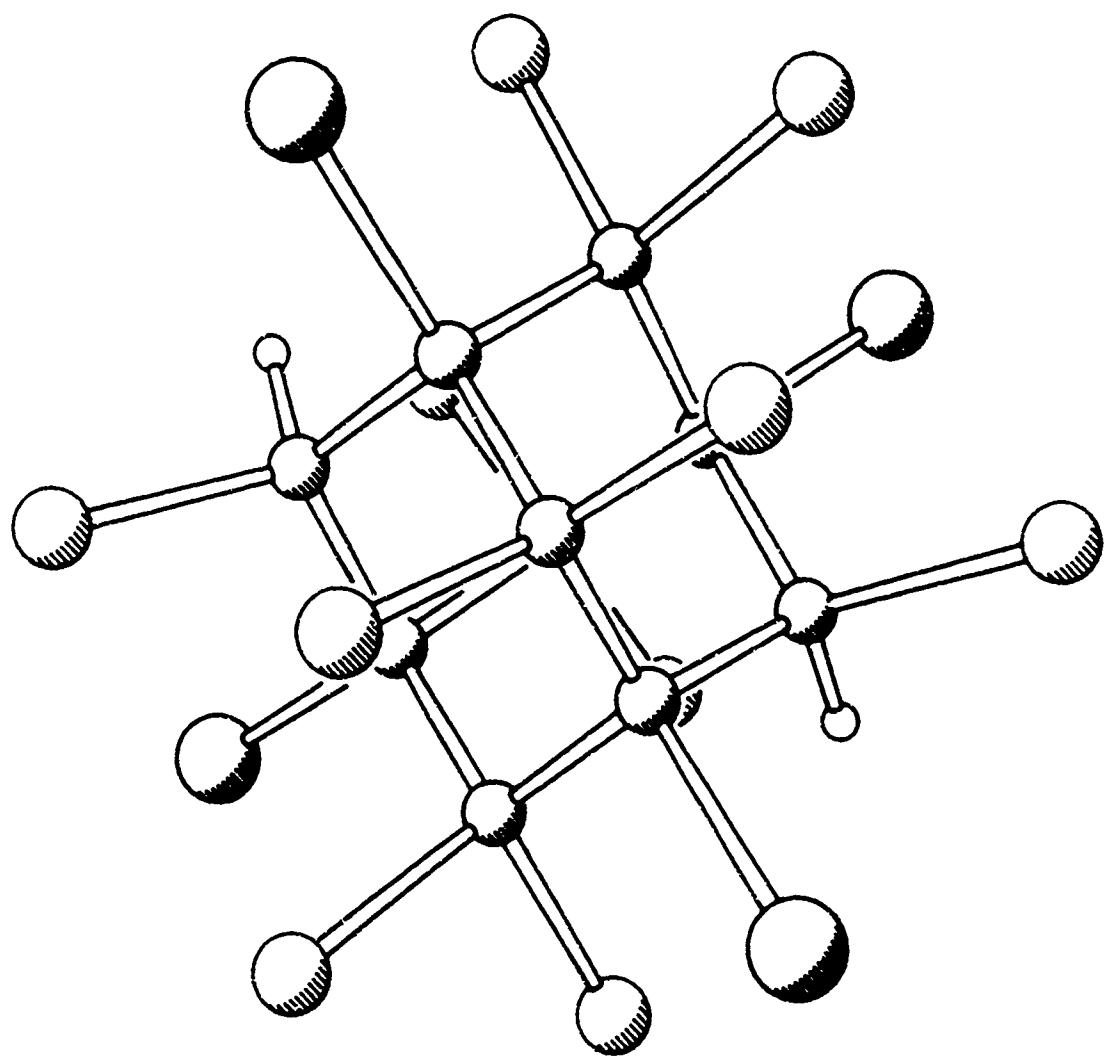
FIGURE 4
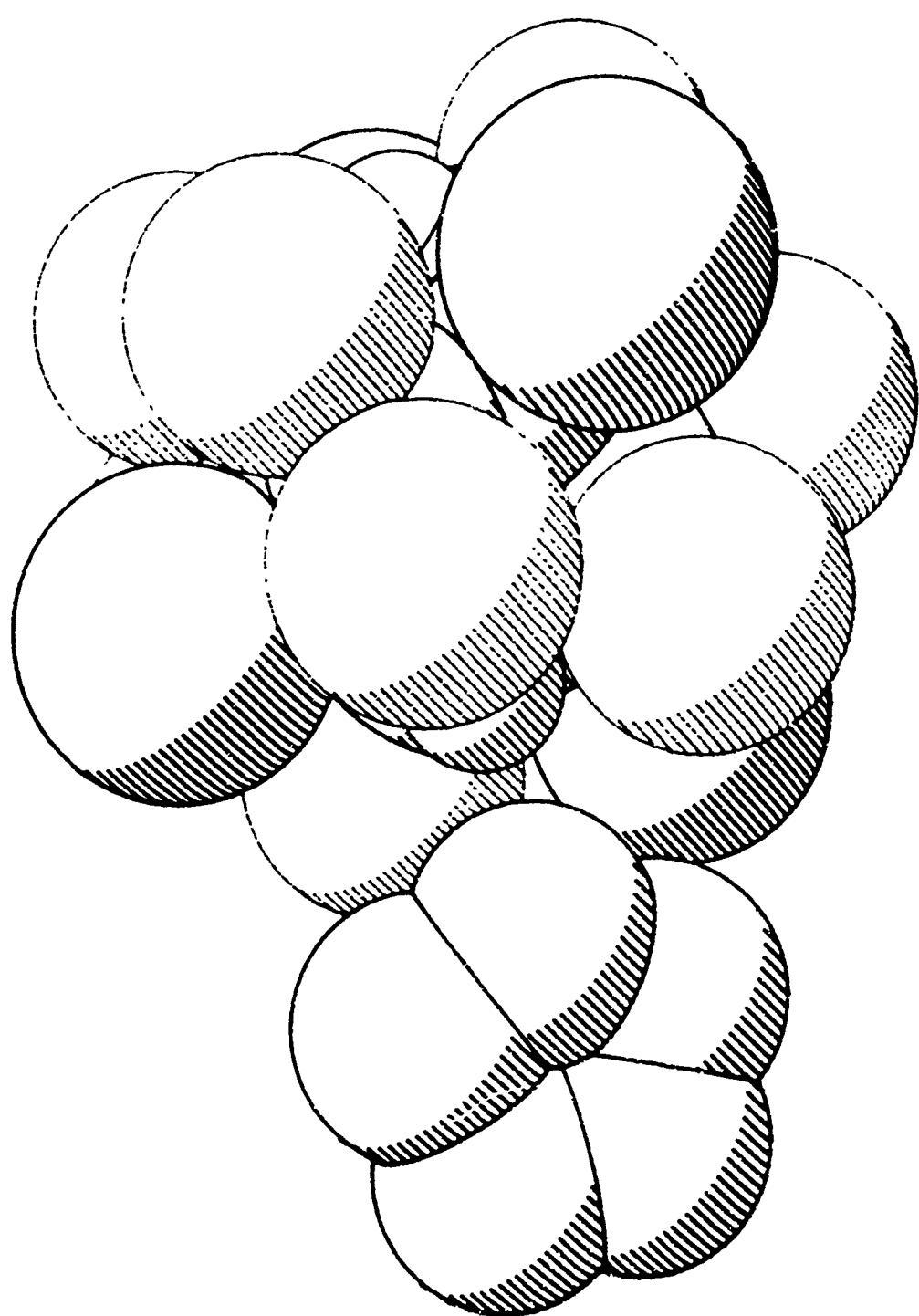
FIGURE 5

FIGURE 6

FIGURE 7

I

C1

C8

C9

C2

C7

C10

C3

F1

C6

C5

C4

F2

F3

I'a

I'b

C1'

C8'

C9'

C2'

C7'

C10'

C3'

F1'

F3'

C6'

C5'

C4'

F2'

I(1)

C(5)

C(2)

C(4a)

I(1a)

C(2a)

C(3)

C(3a)

C(4)

C(1a)

F(1a)

C(1)

C(6)

F(1)